
SORPTION KINETICS OF IONIC DYE FROM AQUEOUS SOLUTION ON BIOMASS FLY ASH

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Summary

The objective of this work was to examine possible application of biomass fly ash (BFA) for removal of ionic, toxic and carcinogenic diazo dye (Congo red) from aqueous solutions. Biomass fly ash is a by-product generated during mixed wood biomass combustion in 1 MW electric power facility in Udbina, Croatia. Batch sorption experiments were carried out to evaluate the influence of experimental parameters such as initial dye concentration (10–80 mg/L) and contact time (0–240 min) on the sorption process. The kinetic experimental data at different initial Congo red (CR) concentrations (20, 40 and 60 mg/L) were fitted by Lagergren's pseudo-first order and Ho's pseudo-second order model. The mechanism of the adsorption process was determined from the intraparticle Weber–Morris diffusion model. Results of the kinetic studies showed that sorption of CR dye onto biomass fly ash was best described by the pseudo-second order kinetic model.

Keywords: sorption kinetics, Congo red, biomass fly ash

Introduction

Wastewater effluents from many industries such as textile, plastic, packed food, pulp and paper, paint, tannery, electroplating, cosmetic, printing etc., contain several kinds of synthetic dyestuffs (Rafatullah et al., 2009). According to an estimate, approximately 10 000 different dyes and pigments are produced commercially worldwide, with an annual production of more than 700 000 tonnes; among them nearly 60%-70% are azo dyes (Shinde and Thorat, 2013). About 5-10% of the dyestuffs are lost in the industrial effluents (Nasuha et al., 2011). There are numerous kinds of dyes with 25 structural classes. The most important of them are azo dyes. Azo dyes are characterized by the presence of one or more chromophoric azo ($R_1-N=N-R_2$) groups and aromatic rings, mostly substituted by sulfonate groups. Azo dyes are highly stable to light, heat, water, detergents, bleach and perspiration due to their resonance and π -conjugated azo bond characteristics. Azo dyes are

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diazotized amines coupled to an amine or phenol, with one or more azo bonds ($-N=N-$). Many of these dyes are extremely toxic, carcinogenic, poisonous and have been known to cause allergic reactions or pose other dangerous threats to human and animal health (Crini, 2006). Therefore, the removal of synthetic dyes with azo aromatic groups from waste effluents is of significant importance for the environment. The dyes have low biodegradability and conventional biological wastewater treatment processes are not efficient in treating dyes present in wastewater (Mondal, 2008). Therefore, dye-wastewater is usually treated by physical and chemical methods, including electrochemical removal (Gupta et al., 2007), electrochemical degradation (Fan et al., 2008), coagulation and flocculation (Zonoozi et al., 2009), membrane separation (Sachdeva et al., 2009), sonochemical degradation (Abbasi and Asl, 2008), photochemical degradation (Sohrabi and Ghavami, 2008), photo-Fenton processes (Gupta et al., 2007), oxidation or ozonation (Malik and Saha, 2003).

The sorption process provides an attractive alternative treatment, especially if the sorbent is inexpensive and readily available (Gupta and Suhas, 2009). Activated carbon is the most popular sorbent, which has been used with great success. However, activated carbon is expensive and its regeneration and reuse make it more costly. In view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost sorbents. According to Bailey et al. 1999 a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal. Such types of sorbents include orange and lemon peels (Rožič et al., 2014), pine tree leaves (Deniz and Karaman, 2011), clays (Auta and Hameed, 2012), rice hull ash (Chou et al., 2001), sugarcane bagasse lignin (Silva et al., 2011), fly ash (Rastogi et al., 2008) etc., which have all been used for the removal of various dyes from wastewaters. However, some of these sorbents do not have good adsorption capacities for anionic dyes because most have hydrophobic or anionic surfaces. Hence, there is a need to find more effective sorbents. In the present study, biomass fly ash was used as sorbent for the removal of CR from its aqueous solutions. The influence of experimental parameters such as contact time and initial CR concentrations was studied. Kinetics of sorption process was evaluated at different initial CR dye concentrations.

Materials and methods

Sorbent - biomass fly ash

All sorption experiments were performed on biomass fly ash (BFA), by-product generated during mixed wood biomass combustion in 1 MW electric power facility in Udbina, Croatia. The amount (wt. %) of main and minor elements in biomass fly ash was

determined by Energy Dispersive X-ray fluorescence spectrometer (EDXRF), EDX-800 HS, Shimadzu, Japan. Concentration (mg/kg) of trace elements in the biomass fly ash was determined, after microwave digestion, by inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC) and atomic absorption spectrometry (AAS AANALYST 600, PERKIN ELMER, SAD). The results of chemical analysis of investigated biomass fly ash are presented in Table 1 and Table 2.

Table 1. Main and minor elements in biomass fly ash (BFA) sample (wt. %)

Sample	TiO ₂	Fe ₂ O ₃	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO
BFA	0.415	3.90	2.05	4.60	2.33	19.1	2.06	1.54	10.2	45.9

Table 2. Concentration (mg/kg) of trace elements in biomass fly ash sample

Sample	Cr	Cu	Zn	Ni	Pb	Cd	As	Hg
BFA	76.4	89.6	102	28.0	13.1	2.38	3.34	0.031

Particle size distribution of biomass fly ash was determined by sieving the sample on an automatic sieve shaker (model AS200 basic, manufacturer Retsch, Germany) through stainless steel sieves using a stack of nested sieves (DIN/ISO 3310-1) with the following aperture size: 32, 50, 63, 125, 212 and 250 µm. The weight of each size fraction was recorded and the percent distribution of weight in each fraction was calculated.

The particle sizes of biomass fly ash were < 32 µm (2.22 wt. %), 32-50 µm (9.52 wt. %), 50-63 µm (2.66 wt. %), 63-125 µm (22.0 wt. %), 125-212 µm (37.9 wt. %), 212-250 µm (8.20 wt. %), and > 250 µm (17.5 wt. %).

Sorbate - Congo red

Congo red contains an azo (-N=N-) chromophore and an acidic auxochrome (-SO₃H) associated with the benzene structure (Fig. 1). The acidic diazo dye Congo red is a sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) (C.I. No. 22120, Direct red 28, formula: C₃₂H₂₂N₆Na₂O₆S₂; molecular weight: 696.66 g/mol).

A stock solution of CR dye was prepared (100 mg/L) by dissolving a required amount of dye powder in deionized water. Experimental solutions of different dye concentrations were prepared by diluting the stock solution with suitable volume of deionized water to obtain desired concentration, ranging from 10 to 80 mg/L.

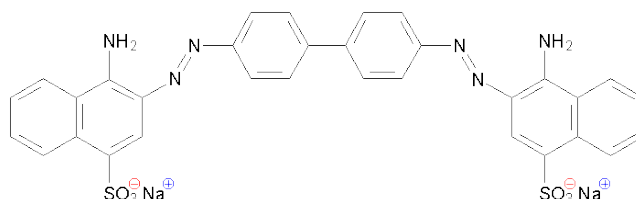


Fig. 1. Molecular structure of Congo red dyestuff

Batch sorption experiments

The sorption of CR on biomass fly ash was investigated in batch mode sorption equilibrium experiments. All batch experiments were carried out in 50 mL flasks containing a fixed amount of sorbent (200 mg) with 50 mL dye solution at a known initial concentration. The flasks were agitated at a constant speed of 300 rpm in an incubator shaker at 25 °C. The influence of contact time (15, 30, 60, 90, 120, 180 and 240 min) and initial dye concentration (10, 20, 40, 50, 60 and 100 mg/L) was evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analysing the residual dye concentration in the solution. Experiments were performed at 25 °C and quantity of CR remaining in the liquid phase after equilibration has been measured by means of UV/VIS spectrophotometer at $\lambda = 498$ nm. All experiments were conducted in triplicate.

In batch equilibrium tests, the difference between the initial and equilibrium mass concentrations of CR is used for calculation of the quantity of CR adsorbed on unit mass of biomass fly ash (BFA) (q , mg CR/g BFA), taking into consideration the data related to the BFA weight, volume and mass concentration of the solution. The amount of CR sorbed onto the biomass fly ash was calculated from the following expression:

$$q_e = \frac{(\gamma_0 - \gamma_e) \cdot V}{m} \quad (1)$$

where q_e is the equilibrium CR concentration sorbed on the biomass fly ash (mg/g), V is the initial volume of the CR solution used (L), m is the mass of biomass fly ash used (g), γ_0 is the initial concentration of CR in the solution (mg/L) and γ_e is the concentration of CR in the solution at equilibrium (mg/L).

The procedure of kinetic sorption tests was identical to that of batch equilibrium tests, however the aqueous samples were taken at preset time intervals. The Congo red (CR) dye sorption at any time, q_t (mg/g), was calculated from the following equation:

$$q_t = \frac{(\gamma_i - \gamma_t)}{m} \cdot V \quad (2)$$

where γ_i (mg/L) is the initial concentration of CR, γ_t (mg/L) is the concentration of CR after period of time t (min); V (L) is the volume of the solution and m (g) is the mass of sorbent.

Results and discussion

Effect of contact time and initial dye concentration

In order to establish the optimal time for maximal removal of Congo red dye by biomass fly ash sorbent, the removal process was studied as a function of contact time. The effect of contact time on the removal of Congo red dye from aqueous solutions was investigated at different initial dye concentration onto BFA sorbent and results are presented in Fig. 2. The process of sorption over time can be described as following two different steps. The first step lasts 15-120 min and is characterised by the gradual increase in the amount of CR removed with increasing reaction time, until an equilibrium is reached. The second step is referring to the complete saturation of the BFA sorbent by the sorbed CR dye molecules: the plots of the three evaluated dye concentrations reached the maximum removal values at 120 min of shaking time.

The results show that sorption process reached equilibrium within 120 minutes. The amount of removed Congo red dye increased from 4.77 mg/g to 10.1 mg/g with increasing initial concentration of CR dye from 20 to 60 mg/L (Fig. 2).

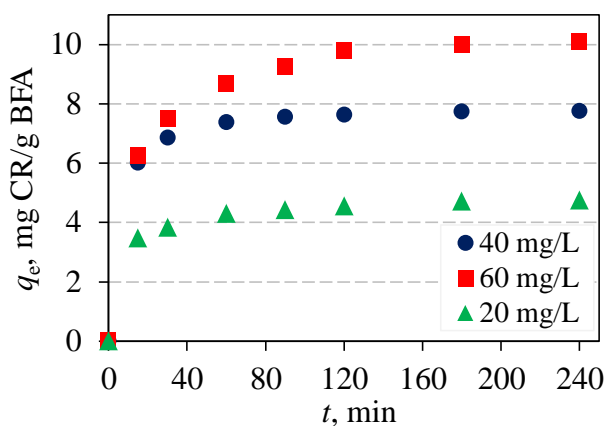


Fig. 2. Effect of contact time on Congo red dye removal by biomass fly ash (BFA) at various initial concentrations. Condition: m (BFA) = 200 mg, V (CR) = 50 mL, agitation speed = 300 rpm, T = 25 °C)

The effect of different initial dye concentrations on adsorption of CR is shown in Fig. 3. It can be seen from the plots of q_e versus γ_e that an increase in initial CR concentration leads to an increase in the adsorption capacity, q_e .

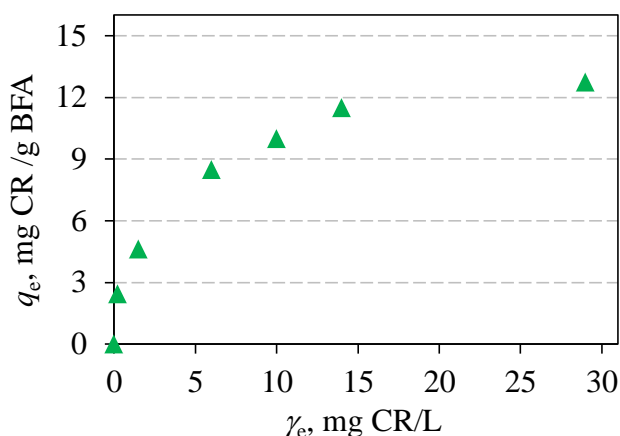


Fig. 3. Effect of initial dye concentration on sorption of Congo red by biomass fly ash (BFA).
Condition: $m(\text{BFA}) = 200$ mg, $V(\text{CR}) = 50$ mL, $t = 120$ min, $T = 25$ °C)

Sorption kinetic studies

Information on the kinetics of CR sorption is required to select the optimal condition for full scale batch CR removal processes. Sorption kinetics depends on the sorbate–sorbent interactions and experimental conditions. The kinetics of CR sorption was investigated by applying pseudo-first order and pseudo-second order model. The pseudo-first order model of Lagergren is described by the following equation (Lagergren and Svenska, 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e and q_t are the amounts of CR, (mg/g) sorbed on sorbent at equilibrium and at time t , respectively and k_1 (min^{-1}) is the rate constant of the pseudo-first order sorption. Integrating Eq. (3) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, yields:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

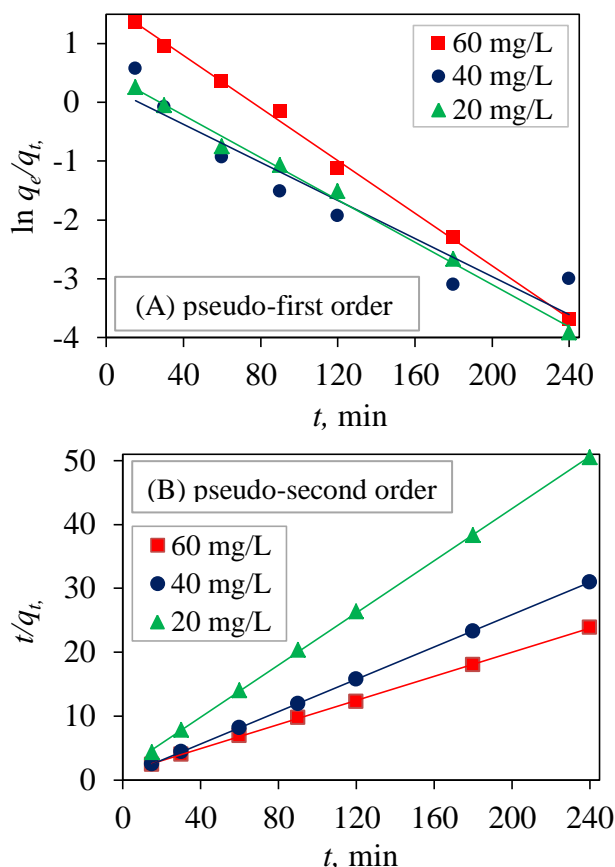


Fig. 4. Sorption of Congo red dye on biomass fly ash (A) pseudo-first order plots and (B) pseudo-second order plots

The kinetic data were further analyzed using Ho's pseudo-second order kinetic model. The pseudo-second order equation is represented as (Ho and McKay, 1998):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where q_e and q_t are the amounts of CR (mg/g) sorbed on sorbent at equilibrium and at time t , respectively and k_2 is the rate constant of pseudo-second order adsorption (mg/g min).

Integrating Eq. (5) for the boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

A plot (Fig. 4 B) of t/q_t against t gives $1/q_e$ as the slope and $1/(k_2 q_e^2)$ as the intercept. The values of q_e , k_1 and R^2 obtained from the linear plots of Eq. (4) and q_e , k_2 and R^2 from the plots of Eq. (6) for the CR sorption on the biomass fly ash are reported in Table 3. It can be seen (Table 3) that for a pseudo-first order model, the linear correlation coefficient (R^2) is less than the pseudo-second order correlation coefficient (R^2). The correlation coefficients for the pseudo-second order kinetic model were very high ($R^2 > 0.99$) and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values at all studied initial CR concentrations. This suggests that the sorption of Congo red on biomass fly ash might be controlled by a mechanism corresponding to the second-order model.

Table 3. The pseudo-first order and pseudo-second order sorption models' constants for Congo red sorption on biomass fly ash.

γ_0 (mg CR/L)	$q_{e, exp}$ ($\mu\text{g/g}$)	Kinetic model					
		Pseudo-first order			Pseudo- second order		
		k_1 (1/min)	$q_{e, cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e, cal}$ (mg/g)	R^2
20	4.77	0.018	1.65	0.9945	0.025	4.89	0.9998
40	7.77	0.020	1.47	0.9426	0.029	7.91	0.9999
60	10.1	0.023	5.39	0.9979	0.008	10.6	0.9997

Sorption mechanism - intraparticle diffusion model

As the above two kinetic models could not definitely reveal the sorption mechanism as well as the rate controlling steps of the sorption process, intraparticle diffusion model according to Weber and Morris (Weber and Morris, 1963) was also applied in the present study. The intraparticle diffusion equation is expressed as:

$$q_t = k_{pi} \sqrt{t} + C_i \quad (7)$$

where k_{pi} (mg/g min^{1/2}), the rate parameter of stage i , is obtained from the slope of the straight line of q_t versus $t^{1/2}$. C_i , the intercept of stage i , gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect. If

intraparticle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved. For a sorbate/sorbent sorption process, the sorbate transfer may include the step of either external mass transfer (film diffusion) or intraparticle diffusion, or both. The intraparticle diffusion plots of q_t against $t^{1/2}$ (Fig. 5) are multi-linear including three linear sections, which indicates that multiple steps take place during adsorption process (Janoš and Šmídová, 2005).

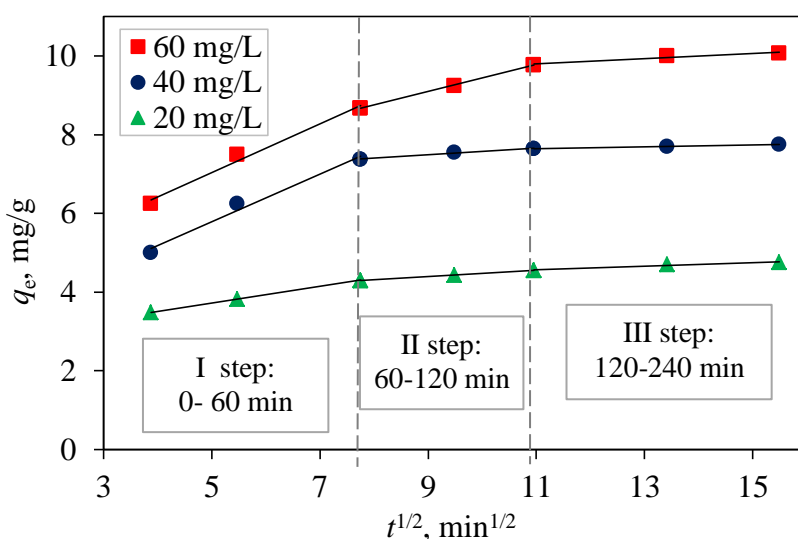


Fig. 5. Plot of intra-particle diffusion model for sorption of Congo red dye onto biomass fly ash at 25 °C

The first stage of sorption (section of the curve with a large slope) corresponds to transport of sorbate from the bulk solution to the external surface of sorbent by film diffusion, which is also called outer diffusion (or boundary layer diffusion). The second stage of sorption describes the gradual adsorption stage, corresponding to the diffusion of the sorbate from the external surface into the pores of the sorbent. This is called intraparticle diffusion or inner diffusion.

The third stage with a small slope indicates the final equilibrium stage: this step is considered to be very fast and thus cannot be treated as the rate-controlling step. Generally, the adsorption rate is controlled by outer diffusion or intra-particle diffusion or both.

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It is clear from Fig. 5 that the rate controlling step of Congo red dye sorption on biomass fly ash involves complex processes, including outer diffusion (film diffusion) and intraparticle diffusion.

The model parameters obtained from the three stages of plots are listed in Table 4.

Table 4. Intraparticle diffusion model constants and correlation coefficients for sorption of Congo red dye on biomass fly ash

q_0 (mg/L)	Intraparticle diffusion								
	First stage of sorption			Second stage of sorption			Third stage of sorption		
	k_{p1} (mg/g min ^{1/2})	C_1	R^2	k_{p2} (mg/g min ^{1/2})	C_2	R^2	k_{p3} (mg/g min ^{1/2})	C_3	R^2
20	0.213	2.65	0.9999	0.078	3.69	0.9976	0.045	4.07	0.9472
40	0.605	2.76	0.9834	0.086	6.72	0.9886	0.022	7.41	0.9970
60	0.619	3.95	0.9865	0.343	9.06	0.9995	0.067	9.06	0.9472

According to intraparticle diffusion model, if the value of C is zero, it means that the rate of sorption is controlled by intraparticle diffusion for the whole sorption period. For all initial concentrations of CR dye, the values of C for each linear stage are not zero (Table 4), indicating that intraparticle diffusion was present as a part of diffusion process, but it is not the only rate-controlling step in all the stages (Toor and Jin, 2012). Additionally, q_t versus $t^{1/2}$ should be linear if intraparticle diffusion was involved in the sorption process.

Conclusions

- The investigation showed that biomass fly ash was a promising low cost sorbent for the removal of ionic, toxic and carcinogenic diazo dye (Congo red) from aqueous solutions over a wide range of concentrations.
- Congo red dye uptake was found to increase with increase in agitation time and CR initial concentration.
- Kinetic results of sorption CR on biomass fly ash were best described by the pseudo-second order kinetic model.
- The sorption of Congo red dye on biomass fly ash occurs through a combination of film and intraparticle mechanism.

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